JAPANESE [JP,2000-230098,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]About an aqueous emulsion composition, in more detail, this invention is excellent in water resistant adhesion, and relates to an aqueous emulsion suitable as the adhesives for woodwork, plywood adhesive, a paint, a textile processing agent, a paper coating agent, etc.
[0002]
[Description of the Prior Art]Conventionally polyvinyl alcohol (it may be hereafter written as PVA) An ethylenic unsaturated monomer, It is widely used as protective colloid for emulsion polymerizations of the vinyl ester system monomer represented by especially vinyl acetate, The vinyl ester system aqueous emulsion produced by carrying out an emulsion polymerization using this as protective colloid For papers, It is widely used in fields, such as the various binders the various adhesives the object for woodwork, for plastics, etc., the object for impregnated papers, for nonwoven products, etc., admixture, ****** material, a paint, paper coating, and textile processing. By making high the saponification degree of the PVA system polymer used as a dispersing agent (protective colloid), a waterproof good thing is obtained comparatively and the object for prizes of such an aqueous emulsion is carried out in the various application as which a water resisting property is required. However, the demand of the further waterproof improvement is called

for in recent years in the exquisite woodwork pasted up using the aqueous emulsion, paper-making products, and an impregnated paper and a textile processing article using this aqueous emulsion as a binder.
[0003]In order to satisfy such a demand, many water resistance-ized techniques by bridge construction by use of the PVA system polymer which introduced the self crosslinkability group, the combination of the aqueous emulsion and cross linking agent which use a cross-linking group introduction PVA system polymer, etc. are proposed, and are put in practical use in part. However, water resistance-ization by such bridge construction is one side although surely there is an effect in waterproof improvement, there is a problem of a preservation stability fall and pot-life shortening at the time of cross linking agent addition, and the actual condition is that it can be incompatible in workability and a water resisting property.
[0004]
[Problem(s) to be Solved by the Invention]It is made in order that this invention may solve the technical problem of the above conventional technologies,There is no problem in preservation stability and pot life, excel in a water resisting property, and The various adhesives the object for papers, the object for woodwork, for plastics, etc., It aims at providing the aqueous emulsion composition suitably used in fields, such as the various binders the object for impregnated papers, for nonwoven products, etc., admixture, ****** material, a paint, paper coating, and textile processing.
[0005]
[Means for Solving the Problem]The above-mentioned purpose makes a dispersoid a polymer which has a kind or two sorts or more of unsaturation monomeric units chosen from an ethylenic unsaturated monomer and a diene system monomer, It is attained by providing an aqueous emulsion composition which consists of an aqueous emulsion (A) and amino group water content nature resin (B) which make a vinyl alcohol system polymer a dispersing agent.
[0006]This invention is explained in detail below. Although a polymer of an ethylenic unsaturated monomer which is a dispersoid in an aqueous emulsion (A) of this invention has various kinds of things, As an ethylenic unsaturated monomer which constitutes this polymer, Olefins, such as ethylene, propylene, and isobutylene, VCM/PVC, Halogenation olefins, such as vinyl fluoridation, vinylidenechloride, and a vinylidenefluoride, Vinyl ester, such as formic acid vinyl, vinyl acetate, vinyl propionate, and BASA tic acid vinyl, Acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, Butyl acrylate, 2-ethylhexyl acrylate, acrylic acid dodecyl, Acrylic ester, such as acrylic acid 2-hydroxyethyl, methyl methacrylate, Ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, Methacrylic acid ester, such as methacrylic acid dodecyl and methacrylic acid 2-hydroxyethyl, Acrylic acid dimethylaminoethyl, dimethylaminoethyl methacrylate and the fourth class ghosts of these and also acrylamide, methacrylamide, N-methylolacrylamide, N,N-dimethylacrylamide, Styrene monomers, such as acrylamide system monomers, such as acrylamide 2-

methylpropanesulfonic acid and its sodium salt, styrene, alpha-methylstyrene, p-styrene sulfonic acid and sodium, and potassium salt, other N-vinyl pyrrolidone, etc. are mentioned. Butadiene, isoprene, chloroprene, etc. are mentioned as a diene system monomer. Independent, two or more sorts are mixed, and these are used. Also in the above-mentioned ethylenic unsaturated monomer, vinyl ester, acrylic ester (meta), styrene, and a diene system monomer are preferred, and concomitant use with vinyl ester, and ethylene and vinyl ester and concomitant use of vinyl ester and acrylic ester (meta) are especially preferred.

[0007]By a publicly known method, a vinyl alcohol system polymer which is a dispersing agent in an aqueous emulsion (A) of this invention is obtained by saponifying a polymer of vinyl ester. As vinyl ester, although formic acid vinyl, vinyl acetate, vinyl propionate, vinyl pivalate, etc. can use, vinyl acetate is usually used from an economic viewpoint.

[0008]If a vinyl alcohol system polymer containing an ethylene unit is used for intramolecular, an effect of this invention will be revealed more notably. A vinyl alcohol system polymer which contains an ethylene unit in intramolecular can be obtained by saponifying a copolymer of vinyl ester and ethylene. Content of ethylene needs to 1-15-mol be %. When it is hard to reveal an effect of ethylene introduction when content of ethylene is less than [1 mol %], and exceeding 15-mol %, the water solubility of a vinyl alcohol system polymer falls, and a stable aqueous emulsion is not obtained.

[0009]Although the amount used in particular to a dispersoid of a vinyl alcohol system polymer which is a dispersing agent is not restricted, it is usually used three to 20% of the weight.

[0010]Although a degree of polymerization of a vinyl alcohol system polymer changes with purposes of use and cannot be defined uniquely, 100 or more are especially preferred and 200-7000 are more preferred. Although there is no restriction in particular also about a saponification degree of this vinyl alcohol system polymer, more than 70 mol % is preferred, and more than 95 mol % is especially more preferred.

[0011]A vinyl alcohol system polymer may comprise a vinyl ester system monomer or a vinyl ester system monomer, and ethylene, is a range which does not spoil an effect of this invention, and may carry out copolymerization of the copolymerizable ethylenic unsaturated monomer. As an ethylenic unsaturated monomer, olefins; acrylic acid, such as propylene, 1-butene, and isobutene, Mono- **** of unsaturation acids, such as methacrylic acid, crotonic acid, fumaric acid, maleic acid (anhydrous), and itaconic acid (anhydrous), a salt of those, or the carbon numbers 1-18 Dialkyl ester; acrylamide, N-alkyl acrylamide of the carbon numbers 1-18, N,N-dimethylacrylamide, Acrylamide, such as 2-acrylamide propanesulfonic acid or its salt, acrylamide propyldimethylamine, its acid chloride, or the 4th class salt of its; Methacrylamide, N-alkyl methacrylamide of the carbon numbers 1-18, N, N-dimethylmethacrylamide, Methacrylamide;N-vinyl pyrrolidone, such as 2-methacrylamide propanesulfonic acid or its salt, methacrylamide

propyldimethylamine, its acid chloride, or the 4th class salt of its, Vinyl cyanides, such as N-vinylamide; acrylonitrile, such as N-vinylformamide and N-vinylacetamide, and a methacrylonitrile; Alkyl vinyl ether of the carbon numbers 1-18, hydroxyalkyl vinyl ether, Vinyl ether, such as alkoxy alkyl vinyl ether; VCM/PVC, Vinylic halide, such as vinylidene chloride and vinyl fluoridation, vinylidene fluoride, and vinyl bromide; Vinylsilane, such as trimethoxy vinylsilane. Allyl acetate, an allyl chloride, allyl alcohol, dimethylallyl alcohol, trimethyl (3-acrylamide 3-dimethylpropyl)-ammonium chloride, an acrylamide 2-methylpropanesulfonic acid salt, etc. are mentioned.

[0012]As amino group water content nature resin (B) which constitutes an aqueous emulsion composition of this invention, (1) vinyl amine system polymer, (2) allylamine system polymer, (3) amino-group content acrylic emulsion, or amino group water content nature acrylic resin is mentioned.

[0013](1) If a vinyl amine system polymer polymerizes and hydrolyzes and obtains N-vinyl amide system monomer, there will be no restriction in particular. As an N-vinyl amide system monomer, it is N-vinylformamide. N-vinylacetamide, an N-methyl-N-vinylformamide, and an N-methyl-N-vinylacetamide are mentioned. In addition to N-vinyl amide system monomer, copolymerization of the ethylenic unsaturated monomers other than N-vinylamide may be carried out in the range which does not influence the feature of a vinyl amine system polymer.

[0014]A vinyl amine system polymer of this invention is obtained by hydrolyzing N-vinyl amide polymer. In order to manufacture N-vinyl amide polymer, N-vinylamide dissolves and especially the precipitation polymerizing method that polymerizes using a radical polymerization initiator in an insoluble organic solvent (it deposits) is preferred for the polymer. As an organic solvent which can be used, under the present circumstances, ethyl acetate, butyl acetate, isopropyl acetate, If benzene, toluene, xylene, ethylbenzene, acetone, methyl ethyl ketone, acetonitrile, methyl pyrrolidone, etc. are the organic solvents which dissolve N-vinylamide and do not dissolve N-vinyl amide polymer, it is usable in all solvents. It is also possible to use these organic solvents, mixing if needed [, such as regulation of a molecular weight,], and it is also possible to use a solvent which dissolves N-vinyl amide polymers, such as water, methanol, and ethanol, carrying out small-quantity (for example, less than 10 % of the weight) mixing. N-vinylamide concentration at the time of polymerizing is usually 5 to 20 % of the weight preferably one to 40% of the weight.

[0015]As long as it dissolves in this organic solvent as a radical polymerization initiator, what kind of compound may be sufficient, If an example is given, azobisisobutyronitrile, 2,2'-azobis (4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis (2,4-dimethylvaleronitrile), 2,2'-azobis (2-methylpropionitrile), 2,2'-azobis (2-methylbutyronitrile), 1,1'-azobis (cyclohexane-1-carbonitrile), There are dimethyl 2,2'-azobis (2-methylpropionate), benzoyl peroxide, tertiary-butyl hydroperoxide, and a thing like JI (2-ethylhexylperoxydicarbonate). An addition of a polymerization initiator is 0.05 to 5 % of the weight preferably 0.01 to

10% of the weight to N-vinylamide. In order to obtain a thing of the moderate target viscosity, chain transfer agents, such as butyl mercaptan, dodecanethiol, bromotrichloromethane, isopropanol, thioglycolic acid, and 2-ethylhexyl thioglycolate, can also be added. Even if it is 0.01 to 5 % of the weight and adds 10% of the weight or more preferably 0.001 to 10% of the weight to N-vinylamide as an addition of a chain transfer agent, the chain transfer effect beyond it is not acquired. As polymerization temperature, it is suitably chosen in the range of the boiling point of an organic solvent used from not less than 30 **. Since it has a long time by end of a polymerization and may become a cause of decline in yield of a polymer when polymerization temperature is too low, not less than 40 ** is the temperature near the boiling point of an organic solvent especially preferably preferably undesirably. It can also polymerize, after deaerating dissolved oxygen in an organic solvent if needed, and especially when polymerizing near the boiling point of an organic solvent, it cannot deaerate but can also polymerize.

[0016]Hydrolysis of N-vinyl amide system polymer can be performed using a basic catalyst or an acid catalyst. Namely, basic catalysts, such as sodium hydroxide, a potassium hydrate, and sodium methylate, Or using acid catalysts, such as p-toluenesulfonic acid, alcohol or glycols, such as methanol, ethanol, propanol, butanol, and ethylene glycol, are used for a solvent, and a hydrolysis reaction is performed. In order to improve the solubility of N-vinyl amide polymer or a catalyst, they are used by solvents, such as a tetrahydrofuran, dioxane, dimethyl sulfoxide, diethylene glycol dimethyl ether, toluene, acetone, and water, mixing suitably. Catalyst concentration / N-vinyl amide monomer unit concentration =0.01-2.0 (mole ratio), reaction temperature of 0-180 **, and a range of conditions of a hydrolysis reaction are usually reaction-time 0.1 to 20 hours.

[0017]More than 0.5 mol % of a hydrolysis degree of N-vinyl amide system polymer is preferred, more than its 1 mol % is more preferred, and more than its 3 mol % is still more preferred. Since there is little amine content of a vinyl amine system polymer obtained when a hydrolysis degree is less than [0.5 mol %], reactivity with a polyurethane prepolymer may become scarce. Although a maximum of a hydrolysis degree does not have restriction in particular, 100% or less and 95 more% or less are preferred.

[0018](2) If it is considered as an allylamine system polymer, as for mono- **** beyond homopolymer;(b)2 sort of a diaryl amine derivative, as for (a) mono- ****, a copolymer of a diaryl amine derivative is mentioned.

[0019]The mono- **** of the above (a) can illustrate polyallylamine, polydiaryl amine, poly (N-benzyldiaryl amine), poly (N-alkyl allylamine), or poly (N-alkyl diaryl amine) as a homopolymer of a diaryl amine derivative. However, an alkyl group of poly (N-alkyl allylamine) or poly (N-alkyl diaryl amine) has methyl, ethyl, hydroxyethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, and a preferred cyclohexyl group.

[0020]Two or more sorts of mono- **** of the above (b) as a copolymer

of a diaryl amine derivative, A copolymer of monoallyl amine and diaryl amine, a copolymer of monoallyl amine and N-alkyl allylamine, A copolymer of monoallyl amine and N-alkyl diaryl amine, a copolymer of diaryl amine and N-alkyl diaryl amine, A copolymer of diaryl amine and N-alkyl allylamine, a copolymer of N-alkyl allylamine and N-alkyl diaryl amine, a copolymer with two or more sorts of N-alkyl allylamines, and a copolymer with two or more sorts of N-alkyl diaryl amine can be illustrated. With however, "alkyl" in the above-mentioned copolymer. Shall understand in a broad sense and Methyl, ethyl, propyl, isopropyl, Aralkyl groups, such as cycloalkyl groups, such as chain alkyl groups, such as sec-butyl and tert-butyl, and cyclohexyl, and benzyl, and an alkyl group which has functional groups, such as a hydroxyl group and a cyano group, further shall be included.

[0021]An amino group content emulsion which has the active hydrogen which denaturalized an acrylic emulsion containing a carboxyl group by alkylene imine as an amino group content acrylic emulsion which has active hydrogen among (3) is illustrated. With an acrylic emulsion containing the above-mentioned carboxyl group. (Meta) Unsaturation monocarboxylic acid, such as acrylic acid, cinnamic acid, and crotonic acid; Itaconic acid, One sort or two sorts or more of monomers chosen from a group of carboxyl group content unsaturated monomers, such as unsaturated-dicarboxylic-acid [, such as maleic acid and fumaric acid,]; or its monoester, A carboxyl group content unsaturated monomer and a copolymerizable monomer. For example, acrylamide (meta), N-methylol (metha)acrylamide, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, Methyl (meta) acrylate, ethyl (meta) acrylate, n-propyl (meta) acrylate, Isopropyl (meta) acrylate, n-butyl (meta) acrylate, Isobutyl (meta) acrylate, t-butyl (meta) acrylate, 2-ethylethyl (meta) acrylate, cyclohexyl (meta) acrylate, stearyl (meta) acrylate, lauryl (meta) acrylate, acrylonitrile (meta), dimethylaminoethyl (meta) acrylate, diethyl ethylamino (meta) acrylate, A method generally known in one sort or two sorts or more of monomers chosen from groups, such as styrene, For example, it is copolymer produced by carrying out an emulsion polymerization underwater by using a vinyl alcohol system polymer as protective colloid under existence of polymerization initiators including potassium persulfate, using emulsifiers including surface-active agents, such as an anionic system and the Nonion system. As a quantity of a carboxyl group, it is required 2% of the weight or more as a monomer, and is 2.5 to 30 % of the weight preferably. In the time of an emulsion polymerization of the above-mentioned [an emulsion containing these carboxyl groups], What constructed the bridge in an inside of an emulsion in monads including divinylbenzene beforehand by a monomer etc. which have two or more copolymerizable unsaturation groups, A thing which controlled a degree of polymerization using chain transfer agents, such as t-dodecyl mercaptan, or a multilayer-structure (core shell type) emulsion obtained by polymerizing two or more sorts of monomers one by one, and a thing by which the emulsion polymerization was further carried out by publicly known methods, such as power feeding, may be used.

[0022]It is amino group water content nature acrylic resin which has the active hydrogen which denaturalized aquosity acrylic resin containing a carboxyl group by alkylene imine as amino group water content nature acrylic resin which has active hydrogen among (3). With aquosity acrylic resin containing a carboxyl group. A kind of a carboxyl group content unsaturated monomer or two sorts or more which indicated an emulsion containing a carboxyl group, It is aqueous resin obtained by carrying out solution polymerization of a kind or two sorts or more of monomers chosen from a group of a carboxyl group content unsaturated monomer and a monomer given [copolymerizable] in the preceding clause, Water solubility or water dispersibility copolymer obtained by solution polymerization with aqueous resin here, Or it is water solubility or water dispersibility resin produced by the copolymer by neutralizing in alkalis, such as amine compounds, such as an alkali, for example, ammonia, trimethylamine, triethylamine, and monoethanolamine, sodium hydroxide, and a potassium hydrate.

[0023]An amino group content acrylic emulsion and aquosity acrylic resin which have the active hydrogen which denaturalized by the above-mentioned alkylene imine, By alkylene imine, it denaturalizes, an acrylic emulsion or aquosity acrylic resin containing the above-mentioned carboxyl group can be compounded, and ethyleneimine, propyleneimine, butylene imine, etc. can be used as alkylene imine, for example. N-(2-amino alkyl) substitution alkylene imine, such as N-(2-aminoethyl) aziridine and N-(2-aminoethyl) propyleneimine, can be used similarly. As an amount of denaturation by alkylene imine, what is necessary is just the range of 0.2 to 5 mol equivalent to a carboxyl group of an acrylic emulsion containing a carboxyl group, or aquosity acrylic resin, and it is 0.5 to 4 mol equivalent preferably. An amino group content acrylic emulsion or aquosity acrylic resin which has active hydrogen which denaturalizes an acrylic emulsion or aquosity acrylic resin containing these carboxyl groups by alkylene imine is independent, or is used as two or more sorts of mixtures.

[0024]In an aqueous emulsion composition of this invention, weight-mix ratio [with amino group water content nature resin (B) which has an aqueous emulsion (A) and active hydrogen] (solid content weight ratio) (A)/(B) is 99.9 / 0.1 - 50/50, and is 99.8 / 0.2 - 70/30 preferably. (A) When / (B) exceeds 99.9/0.1, a water resistance-ized effect is low, and when it is less than 50/50, the viscosity stability of an aqueous emulsion composition may fall.

[0025]In order to prepare the drying property, set nature, viscosity, film formability, etc. if needed, an aqueous emulsion composition of this invention, Various organic solvents, such as toluene, a perchloroethylene, dichlorobenzene, and trichlorobenzene, Starch, denaturation starch, oxidation starch, sodium alginate, carboxymethyl cellulose, Methyl cellulose, hydroxymethylcellulose, a maleic anhydride/ isobutene copolymer, A maleic anhydride/styrene copolymer, a maleic anhydride / methyl-vinyl-ether copolymer, Water soluble polymers, and urea/formalin resin, such as polyvinyl alcohol, Thermosetting resin, such as urea / melamine / HORIMARIN resin, phenol / HORIMARIN resin,

Paints or things which, in addition to this, contain various additive agents, such as a defoaming agent, a dispersing agent, an antifreeze, an antiseptic, and a rust-proofer, such as extenders, such as bulking agents, such as clay, kaolin, talc, calcium carbonate, and wood flour, and wheat flour, and titanium oxide, may be used. In various applications, such as adhesives for woodwork, adhesives for paper coatings, a paint, and a textiles processing agent, an aqueous emulsion composition of this invention is used taking advantage of the feature that a water resisting property is high.

[0026]

[Example]Although an example and a comparative example are given and this invention is explained concretely hereafter, this invention is not limited at all by these. A weight reference is meant unless it refuses especially a "part" and"%" in the following examples and comparative examples.

[0027]The example 1 (example of manufacture of a vinyl amine system polymer) of manufacture

100 copies of N-vinylacetamides were melted in 900 copies of ethyl acetate, this was boiled, 0.002 copy of azobisisobutyronitrile was added as a radical polymerization initiator, and the state of boil was maintained as it was. Since generated N-vinyl amide polymer deposited in ethyl acetate as the polymerization advanced, it held as it is for 3 hours. Suction filtration of the radiational-cooling postpolymerization object was carried out, and 50 ** of impalpable powder-like N-vinylacetamide polymers [98 copies of] were obtained by carrying out vacuum drying for 24 hours, and cracking.

[0028]Ten copies of this N-vinylacetamide polymer was dissolved in 50 copies of methanol, and temperature up was carried out to 60 **. 20 copies of 10% of sodium hydroxide methanol solution was added to this solution, and it hydrolyzed into it by stirring for 2 hours. When the hydrolysis degree of the obtained vinyl amine system polymer (polyamine 1) was measured by conductometric titration, it was 83-mol %.

[0029]The example 2 (example of manufacture of an amino group content acrylic emulsion) of manufacture

Temperature up was carried out to 68 **, carrying out nitrogen bubbling, after teaching 780 copies of ion exchange water, and 75 copies of anionic system surface-active agents (25% solution) to a separable flask with a provided with an agitator, the reflux condenser, the thermometer, the nitrogen introducing pipe, and the dropping funnel capacity of 2 l. 90 copies of acrylic acid, 100 copies of methyl methacrylate, and 200 copies of butyl acrylates, After adding the polymerization nature monomeric mixture which consists of 350 copies of styrene in an 80-copy flask and performing stirring for 30 minutes, 2% of the weight of hydrogen peroxide solution [eight copies of] and eight copies of 2-% of the weight L-ascorbic acid solution were added, and the polymerization was started. The remaining polymerization nature monomeric mixtures were uniformly dropped over 90 minutes after [of the polymerization start] 15 minutes. 2% of the weight of hydrogen peroxide solution [80 copies

of] and 70 copies of 2-% of the weight L-ascorbic acid solution were divided till the end of dropping of a polymerization nature monomeric mixture every 10 minutes in the meantime, and it was dropped in the flask. After the end of dropping, aging was performed for 1 hour, it cooled, and the emulsion of 45 % of the weight of nonvolatile matters was obtained. Next, it added under stirring of 32 copies of 17-% of the weight ethyleneimine solution to emulsion 150 weight section, the reaction was performed at 50 ** for 2 hours, and 0.188 mol of amino groups/100g emulsion solid content weight, and the amino group content acrylic emulsion (polyamine 2) of 41 % of the weight of nonvolatile matters were obtained.

[0030]100 copies of ion exchange water and PVA-117(degree-of-polymerization 1700, 98.5% of saponification degree)5 copy were taught to example of aqueous emulsion manufacture 1 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth, and it dissolved in them thoroughly at 95 **. Next, after teaching ten copies of vinyl acetate and carrying out temperature up to 60 **, agitating this PVA solution at 140 rpm after cooling and a nitrogen purge, the polymerization was started under existence of the redox initiator system of hydrogen peroxide/ tartaric acid. 90 copies of vinyl acetate was continuously added over 3 hours after [of the polymerization start] 15 minutes, and the polymerization was completed. The polyvinyl acetate emulsion of 48.5% of solids concentration was obtained. Addition mixing of five copies of dibutyl phthalates was carried out to 100 weight sections of this emulsion (Em-1).

[0031]100 copies of ion exchange water and PVA-217(degree-of-polymerization 1700, 88% of saponification degree)5 copy were taught to example of aqueous emulsion manufacture 2 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth, and it dissolved in them thoroughly at 95 **. Next, after teaching ten copies of vinyl acetate and carrying out temperature up to 60 **, agitating this PVA solution at 140 rpm after cooling and a nitrogen purge, the polymerization was started under existence of the redox initiator system of hydrogen peroxide/ tartaric acid. 90 copies of vinyl acetate was continuously added over 3 hours after [of the polymerization start] 15 minutes, and the polymerization was completed. The polyvinyl acetate emulsion of 48.5% of solids concentration was obtained. Addition mixing of five copies of dibutyl phthalates was carried out to 100 weight sections of this emulsion (Em-2).

[0032]To example of aqueous emulsion manufacture 3 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth. 100 copies of ion-exchange-water, degree-of-polymerization 1700, saponification degree [of 98.5%], and amount% of 2.5 mol of ethylene denaturation of vinyl alcohol system polymers [five copies of] were prepared, and it dissolved thoroughly at 95 **. Next, after teaching ten copies of vinyl acetate and carrying out temperature up to 60 **, agitating this PVA

solution at 140 rpm after cooling and a nitrogen purge, the polymerization was started under existence of the redox initiator system of hydrogen peroxide/tartaric acid. 90 copies of vinyl acetate was continuously added over 3 hours after [of the polymerization start] 15 minutes, and the polymerization was completed. The polyvinyl acetate emulsion of 48.5% of solids concentration was obtained. Addition mixing of five copies of dibutyl phthalates was carried out to 100 weight sections of this emulsion (Em-3).

[0033]Em-1 obtained in the example 1 of example 1 aqueous-emulsion manufacture Five weight sections of polyamine 1 obtained in the example 1 of manufacture was blended to 100 weight sections, and the aqueous emulsion composition was adjusted. The following way estimated the coat water resisting property, water resistant adhesion, and viscosity stability of the obtained aqueous emulsion composition. A result is shown in Table 1.

[0034](Evaluation of an emulsion)

(1) Under 20 **65%RH, the waterproof profitable **** aqueous emulsion of the coat was cast on PET, was dried for seven days, and a 500-micrometer dry film was obtained. This coat was pierced in diameter of 2.5 cm, and it asked for the water absorption of a coat at the time of being immersed in 20 ** water by making it into a sample for 24 hours, and an elution rate.

(2) The water-resistant-adhesion profitable **** aqueous emulsion was 150-g/m-^{2}-applied to the hemlock fir (straight wood grain), was pasted together, and it pressed by the load of 7 kg/m^2 for 16 hours. Then, after decompressing and recuperating oneself for five days under 20 **65% RH, it was immersed in 60 ** warm water for 3 hours, and the compression shear strength was measured in the state where it has wetted wet.

(3) Viscosity change 30 days after [at the time of neglecting a viscosity stability emulsion at 5 ** and 50 **] was observed.

[0035]**** for 5 weight sections examined the polyamine 2 obtained in the example 2 of manufacture like Example 1 instead of using the polyamine 1 used in example 2 Example 1. A result is collectively shown in Table 1.

[0036]**** for 5 weight sections examined polyallylamine (the Nitto Boseki Co., Ltd. make, molecular weight 10000) like Example 1 instead of using the polyamine 1 used in example 3 Example 1. A result is collectively shown in Table 1.

[0037]0.5 copy of example 4 polyamine 1 was used, and also it examined like Example 1. A result is collectively shown in Table 1.

[0038]30 copies of example 5 polyamine 1 was used, and also it examined like Example 1. A result is collectively shown in Table 1.

[0039]It examined like Example 1 except not using the polyamine 1 used in comparative example 1 Example 1. A result is collectively shown in Table 1.

[0040]Em-2 obtained in the example 2 of aqueous emulsion manufacture was used instead of using Em-1 obtained in the example 1 of aqueous emulsion manufacture used in example 6 Example 1, and also it

examined like Example 1. A result is collectively shown in Table 1.
[0041]It examined like Example 6 except not using the polyamine 1 used in comparative example 2 Example 6. A result is collectively shown in Table 1.
[0042]Em-3 obtained in the example 3 of aqueous emulsion manufacture was used instead of using Em-1 obtained in the example 1 of aqueous emulsion manufacture used in example 7 Example 1, and also it examined like Example 1. A result is collectively shown in Table 1.
[0043]It examined like Example 7 except not using the polyamine 1 used in comparative example 3 Example 7. A result is collectively shown in Table 1.
[0044]PVA217 (degree-of-polymerization 1700 and saponification degree % of 88 mol) to a dispersoid as an ethylene-vinylacetate copolymer emulsion {dispersing agent instead of using Em-1 obtained in the example 1 of aqueous emulsion manufacture used in example 8 Example 1 5% content, 55% of solids concentration, Em-4} was used and also it examined like Example 1. A result is collectively shown in Table 1.
[0045]It examined like Example 8 except not using the polyamine 1 used in comparative example 4 Example 8. A result is collectively shown in Table 1.
[0046]To comparative example 5 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth. 100 copies of ion exchange water, acetoacetyl groups denaturation PVA (degree-of-polymerization 1030, saponification degree [of 98.5%], and amount% of 5.0 mol of acetoacetyl groups denaturation of vinyl alcohol system polymers [five copies of] were prepared, and it dissolved thoroughly at 95 **.) Next, after teaching ten copies of vinyl acetate and carrying out temperature up to 60 **, agitating this PVA solution at 140 rpm after cooling and a nitrogen purge, the polymerization was started under existence of the redox initiator system of hydrogen peroxide/tartaric acid. 90 copies of vinyl acetate was continuously added over 3 hours after [of the polymerization start] 15 minutes, and the polymerization was completed. The polyvinyl acetate emulsion of 48.4% of solids concentration was obtained. Addition mixing of five copies of dibutyl phthalates was carried out to 100 weight sections of this emulsion (Em-5). "Em-5" obtained To 100 weight sections, five weight sections of glyoxal solution was blended 40%, and the aqueous emulsion composition was adjusted. The same way as Example 1 estimated the coat water resisting property, water resistant adhesion, and viscosity stability of the obtained aqueous emulsion composition. A result is collectively shown in Table 1.
[0047]
[Table 1]

(A)(部)	(B)(部)	皮膜の耐水性		耐水接着力	粘度安定性	
		吸水率(%)	膨潤率(%)	(kg/cm²)	5℃	50℃
実施例1 Em-1 100	(1) 5	30.6	6.3	14	変化なし	変化なし
2 Em-1 100	(2) 5	29.7	6.2	15	変化なし	変化なし
3 Em-1 100	(3) 5	29.5	6.2	15	変化なし	変化なし
4 Em-1 100	(1) 0.5	32.0	6.6	10	変化なし	変化なし
5 Em-1 100	(1)30	29.8	6.1	16	変化なし	変化なし
比較例1 Em-1 100	なし	35.2	7.3	2	変化なし	変化なし
実施例6 Em-2 100	(1) 5	33.6	7.1	12	変化なし	変化なし
比較例2 Em-2 100	なし	38.4	8.2	7	変化なし	変化なし
実施例7 Em-3 100	(1) 5	28.7	5.4	26	変化なし	変化なし
比較例3 Em-3 100	なし	32.6	6.3	7	変化なし	変化なし
実施例8 Em-4 100	(1) 5	21.0	2.5	18	変化なし	変化なし
比較例4 Em-4 100	なし	23.7	3.4	6	変化なし	変化なし
比較例5 Em-5 100	Gox	29.7	6.2	15	増粘(約2倍)	ゲル化

Em－1：ポリ酢酸ビニルエマルジョン（ＰＶＡ－１１７分散剤、固形分濃度４８．５％）
Em－2：ポリ酢酸ビニルエマルジョン（ＰＶＡ－２１７分散剤、固形分濃度４８．５％）
Em－3：ポリ酢酸ビニルエマルジョン（エチレン変性ビニルアルコール系重合体分散剤、固形分濃度４８．５％）
Em－4：エチレン－酢酸ビニル共重合体エマルジョン（ＰＶＡ—２１７分散剤、固形分濃度５５％）
Gox　　：４０％グリオキザール水溶液

[0048]
[Effect of the Invention]The aqueous emulsion composition of this invention is excellent in neglect viscosity stability, and also it is excellent in water resistant adhesion.
It is broadly used for the adhesives for woodwork, plywood adhesive, a paper coating agent, a paint, a textile processing agent, etc. suitably.

[Translation done.]